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EVAPORATION OF SEMICONDUCTORS

by

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ABSTRACT

A series of tests are described wherein attempts were made to produce evaporated semiconductor films which might be used as crystal rectifiers. Although a large range of evaporation pressures, impurities, surfaces and heat treatments were used, no film could be produced having desired front-to-back resistance ratios. These unfavorable results are interpreted and confirmed by x-ray diffraction patterns as being due to the invarying polycrystalline rather than single crystal structure of the film.

I. PURPOSE OF INVESTIGATION

This research was undertaken to study some of the properties of evaporated semiconductor films with a view toward producing crystal rectifiers by evaporation which might be used as non-linear elements in millimeter wavelength harmonic generators.

II. SUMMARY OF ACTIVITIES PRIOR TO RESEARCH

Before this research was undertaken, it was believed that a valuable method of crystal production would be realized if it were possible to evaporate a layer of n-type semiconductor on a base, and immediately afterward evaporate a layer of p-type semiconductor over the n-type layer thus producing a n-p junction. Rectifiers and transistors could be produced readily if this process proved to be feasible.

Library research showed that relatively little had been published on evaporation of metals and practically nothing had been published on the evaporation of semiconductors.

Before this project could rightfully be undertaken, it was necessary to determine if the film of semiconductor had a crystalline structure. If this film was completely amorphous there would be no need for further investigation. Thus, in a preliminary test, a small amount of germanium was evaporated in a vacuum chamber and collected on a glass microscope slide. An x-ray diffraction pattern of this evaporated germanium film gave some indication of a crystalline structure, and it was on this evidence that the research was undertaken.

III. SEMICONDUCTORS AND IMPURITIES INVESTIGATED

Most of the work in this investigation was performed with germanium as the semiconductor. Germanium was picked over silicon primarily because of its lower melting point and because of the more favorable characteristics of germanium during evaporation. Silicon has the unfortunate property of reacting with most metal filaments or evaporation boats and burning up the metal.

The germanium used was 99.99+% pure and extreme care was maintained during all operations in order to exclude any unwanted impurities. The impurities which were deliberately added to the pure germanium came from Group III or Group V of the periodic table. Boron, aluminum, bismuth and antimony were tried as the desired impurity during the course of the investigation.

IV. EQUIPMENT

Throughout the investigation the semiconductor was evaporated in a large bell jar 18 inches in diameter and 18 inches tall. Provisions were made to allow electrical connections to be brought into the evacuation chamber. The vacuum system was able to maintain a pressure of 5×10^{-5} mm of Hg by using a combination of a mechanical pump and an oil-diffusion pump. Most of the evaporation was performed at a pressure of 10^{-4} mm of Hg. Some trials were, however, made with chamber pressures varying from 10^{-2} to 5×10^{-5} mm Hg. No appreciable difference in results could be detected as the pressure varied from 5×10^{-3} to 5×10^{-5} mm of Hg.

Most of the evaporation was performed by passing heavy currents through tantalum evaporation boats until the desired temperature was reached. Many evaporation techniques were tried, but few gave results equal to those involving the tantalum evaporation boat.

V. TECHNIQUE OF IMPURITY ADDITION

Two methods were tried for the addition of the desired impurity to the pure germanium. One method involved the accurate weighing of a known quantity of germanium and a known quantity of impurity, melting these two substances into a common melt in a helium atmosphere, and finally evaporating the mixture in the evacuated bell jar. This method had the advantage of determining the ratio of semiconductor to impurity with fair accuracy, but had the disadvantage of allowing one substance to evaporate before the other if their evaporation temperatures differed very much. (The evaporation temperature referred to here is the temperature at which the vapor pressure equals the pressure in the vacuum chamber.) The only satisfactory solution for this problem was to choose an impurity whose evaporation temperature was near that of the semiconductor and then heat the evaporation container as rapidly as possible so that the evaporation temperature of both substances was reached at very nearly the same time.

The other method used for the addition of the desired impurity made use of two separate evaporation boats—one for the semiconductor and one for the desired impurity. This technique required that a knowledge of the evaporation rate be known for each substance. This was obtained as follows: a tungsten wire was spot welded to the middle of each tantalum evaporation boat, and the thermocouple thus formed provided a method of determining the temperature of each boat. This thermocouple was calibrated with the aid of an optical pyrometer. Several tests were made for each material to be evaporated, and by carefully weighing before and after evaporation it was possible to draw a graph of evaporation versus temperature for a given length of time. This technique was considerably more time consuming but proved to be the only satisfactory method for evaporating two substances whose evaporation temperatures were significantly different.

VI. METHODS OF TESTING THE EVAPORATED FILMS

Originally it was planned to test each evaporated semiconductor film for resistance and front-to-back ratio with direct current, then to investigate the properties at radio frequencies. As it turned out, the results were unfavorable even for the direct current tests so that only a limited number of trials were conducted at radio frequencies.

As a method of comparing the resistance of the evaporated films the unit "per square" was used, i.e., the resistance exhibited by the film across a square. Obviously, the film thickness influenced the resistance per square. This method, however, afforded a measure of comparison between films. The film thickness throughout this investigation was estimated to be in the neighborhood of 500 to 1000 angstroms thick. A discussion of the resistances per square will be made later.

The front-to-back ratio was determined by bringing a tungsten wire cat-whisker in contact with the evaporated film and a resistance check made with the whisker positive and again with the whisker negative. In this manner it was possible to see if the film favored one polarity more than the other, thus showing signs of rectification.

Various size tungsten whiskers were tried, varying from 0.0009 inch to 0.005 inch in diameter. All whiskers were pointed and polished by an electrolytic process.¹ No conclusions could be drawn as to the best whisker size.

VII. RESULTS OF TESTS

Antimony was tried as an impurity for germanium in a large number of trials. The antimony content varied from 0.05 per cent by weight up to 1.00 per cent.

¹ Henry C. Torrey and Charles A. Whitmer, Crystal Rectifiers, page 318, McGraw Hill, 1948.

Early investigations using approximately 0.05 per cent antimony gave evaporated film resistances in the order of 500 megohms per square. There was no measurable front-to-back resistance indicated in the whisker test. It was believed that the lack of front-to-back ratio was due to the masking caused by the extremely high resistance, and it was felt that the extremely high resistance was caused by the lack of current carriers in the germanium crystal structure. Obviously, the addition of more antimony would provide the current carriers needed. Many tests followed with the content of antimony increased each time. The increase in impurity served to lower the resistance of the film, and a front-to-back ratio began to appear with antimony content somewhere around 0.1%. This front-to-back ratio at best was never better than 1 megohm in the forward direction and about 8 megohms in the reverse direction.

The position of the whisker, and the variation of the pressure seemed to give wide variations in the front-to-back ratio. The wide variation in whisker position indicated an extremely polycrystalline film and this was later confirmed in a series of x-ray tests.

It was soon demonstrated that the addition of impurities could not be carried far enough to give a resistance low enough to provide a workable rectifier. It is well known that the contact potential difference between a metal and a semiconductor is of the greatest importance in the theory of rectification, and this difference in potential is essential to rectification. The contact potential difference between a metal and a semiconductor is also approximately equal to the difference in their work functions, and the work function of a semiconductor depends on the amount and type of impurities present. As the amount of antimony was increased, the work function changed and eventually the front-to-back ratio was lost. This loss of rectification occurred before the resistance of the film could be brought into a workable range.

The experiments with antimony are typical of the results obtained with the other impurities tried. Tests were made with aluminum and bismuth content ranging from 0.05% to 1.00% and boron content ranging from 0.005% to 0.10% by weight. Results were similar to the experiments previously described and none showed promise of producing a satisfactory rectifier film.

Many experiments were conducted with various materials used as a base on which the germanium plus impurity were condensed. Glass, nickel, copper and germanium were tried. These experiments indicated the base material influenced the structure of the film. Tests showed, however, that a single-crystal film could not be produced by condensing the evaporated semiconductor on a seed with a desired crystal orientation. It is believed that the molecules of the semiconductor condense in an extremely short time before they can fully orientate themselves, even though a seed with a desired orientation is provided. It should be stated, however, that the crystal growth in an evaporated film exhibited a preferred orientation, but it was far from a single crystal layer.

Many heat treatments were conducted varying from 500 degrees Centigrade up to 1000 degrees Centigrade and extending from short periods of time up to 48 hours in length. These experiments were primarily conducted to try to find a way of converting the polycrystalline film to a single crystal layer. No technique was found that would accomplish this. As a by-product of these tests, it was found

that a n-type germanium film could be converted to a p-type germanium film by application of heat. A full investigation of this effect was not undertaken, but the change was noticed during one test where a layer was heated at 500 degrees Centigrade for 10 hours. It is believed the change would take place in a much shorter time because of the small dimensions of the film.

VIII. ADDITIONAL STUDIES MADE ON FILMS

It was realized at the outset of the investigation that a clear understanding of the structure of the film would have to be determined before any final conclusions could be reached. Considerable time was spent in trying to examine the surface of the evaporated films. The structure of the surface proved to be so fine that replicas of the film surface, properly shadowed and magnified up to 100,000 times with an electron microscope, failed to indicate any significant information.

Transmission type electron diffraction patterns were not too satisfactory either, because the film used for the diffraction pattern had to be made thinner than the usual rectifier film so that the electron beam of the electron microscope could satisfactorily penetrate the film. Since it was found that the structure of the film was influenced by the surface on which the molecules condensed, it was believed that an analysis made of a transmission type diffraction pattern of a thin film would not necessarily represent the analysis of a thick film. Later, efforts were made to produce reflection-type diffraction patterns, but satisfactory patterns could not be obtained and no information could be learned from this source.

As a final source of information, x-ray diffraction patterns were made of the evaporated films, and a detailed study was undertaken. These studies revealed that the film does contain extremely fine crystals and the film is very polycrystalline in nature.

IX. CONCLUSIONS

The results of the x-ray diffraction studies along with the results of all the other tests indicate that an evaporated semiconductor film does not provide a suitable means for producing ideal rectifiers. This failure is primarily due to the extreme polycrystalline nature of the evaporated film. Each boundary layer between the many fine crystal growths represents an uncontrollable surface in a film where complete control is desired.

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